



OXYGEN SENSOR

Patent number: EP0770211
Publication date: 1997-05-02
Inventor: RADFORD RICHARD (GB); PEEL DAVID (GB); BAKER DAVID (GB)
Applicant: RADFORD RICHARD (GB); PEEL DAVID (GB); BAKER DAVID (GB)
Classification:
- **international:** G01N27/416
- **european:** G01N27/416D; G01N27/49B
Application number: EP19960913638 19960509
Priority number(s): WO1996GB01110 19960509; GB19950009549 19950511

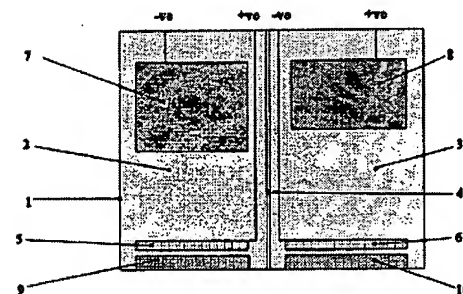
Also published as:

 WO9635944 (A1)
 EP0770211 (B1)

Abstract not available for EP0770211

Abstract of corresponding document: **WO9635944**

An oxygen sensor arrangement (1), based upon galvanic fuel cell technology, consisting of a measuring (2) and a monitoring (3) element, whereby the monitoring element (3) is designed, by virtue of a reduced surface area of monitoring anode material, to fail before the measuring element. The premature failure of the monitoring element providing an ability, at points determined by suitable electronic comparator circuits, to alert the user to the impending failure of the measuring element and/or disable the measuring element, before the measuring element itself fails.

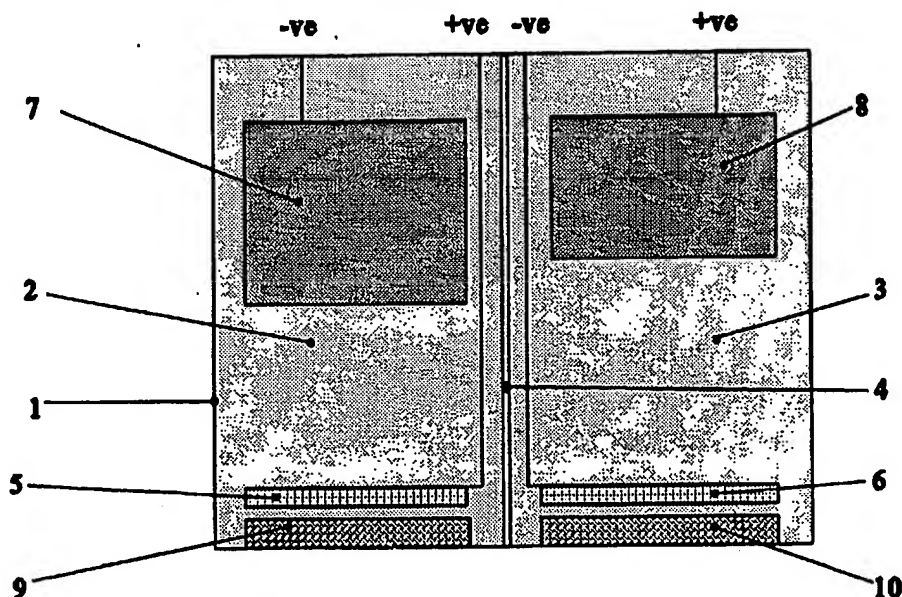


Data supplied from the esp@cenet database - Worldwide

INTERNATIONAL APPLICATION PUBLISHED UNDER THE PATENT COOPERATION TREATY (PCT)

(51) International Patent Classification ⁶ : G01N 27/416	A1	(11) International Publication Number: WO 96/35944 (43) International Publication Date: 14 November 1996 (14.11.96)
<p>(21) International Application Number: PCT/GB96/01110</p> <p>(22) International Filing Date: 9 May 1996 (09.05.96)</p> <p>(30) Priority Data: 9509549.3 11 May 1995 (11.05.95) GB</p> <p>(71)(72) Applicants and Inventors: RADFORD, Richard [GB/GB]; 53 Pocklington Crescent, Winthorpe, Newark, Notts. NG24 2PG (GB). PEEL, David [GB/GB]; 12 Riverside, Southwell, Notts. NG25 0HA (GB). BAKER, David [GB/GB]; 1 Bird Close, Kingshaven, Mansfield, Notts. NG18 4AZ (GB).</p>	<p>(81) Designated States: AL, AM, AT, AU, AZ, BB, BG, BR, BY, CA, CH, CN, CZ, DE, DK, EE, ES, FI, GB, GE, HU, IS, JP, KE, KG, KP, KR, KZ, LK, LR, LS, LT, LU, LV, MD, MG, MK, MN, MW, MX, NO, NZ, PL, PT, RO, RU, SD, SE, SG, SI, SK, TJ, TM, TR, TT, UA, UG, US, UZ, VN, ARIPO patent (KE, LS, MW, SD, SZ, UG), Eurasian patent (AM, AZ, BY, KG, KZ, MD, RU, TJ, TM), European patent (AT, BE, CH, DE, DK, ES, FI, FR, GB, GR, IE, IT, LU, MC, NL, PT, SE), OAPI patent (BF, BJ, CF, CG, CI, CM, GA, GN, ML, MR, NE, SN, TD, TG).</p> <p>Published With international search report. Before the expiration of the time limit for amending the claims and to be republished in the event of the receipt of amendments.</p>	

(54) Title: OXYGEN SENSOR



(57) Abstract

An oxygen sensor arrangement (1), based upon galvanic fuel cell technology, consisting of a measuring (2) and a monitoring (3) element, whereby the monitoring element (3) is designed, by virtue of a reduced surface area of monitoring anode material, to fail before the measuring element. The premature failure of the monitoring element providing an ability, at points determined by suitable electronic comparator circuits, to alert the user to the impending failure of the measuring element and/or disable the measuring element, before the measuring element itself fails.

FOR THE PURPOSES OF INFORMATION ONLY

Codes used to identify States party to the PCT on the front pages of pamphlets publishing international applications under the PCT.

AM	Armenia	GB	United Kingdom	MW	Malawi
AT	Austria	GE	Georgia	MX	Mexico
AU	Australia	GN	Guinea	NE	Niger
BB	Barbados	GR	Greece	NL	Netherlands
BE	Belgium	HU	Hungary	NO	Norway
BF	Burkina Faso	IE	Ireland	NZ	New Zealand
BG	Bulgaria	IT	Italy	PL	Poland
BJ	Benin	JP	Japan	PT	Portugal
BR	Brazil	KE	Kenya	RO	Romania
BY	Belarus	KG	Kyrgyzstan	RU	Russian Federation
CA	Canada	KP	Democratic People's Republic of Korea	SD	Sudan
CF	Central African Republic	KR	Republic of Korea	SE	Sweden
CG	Congo	KZ	Kazakhstan	SG	Singapore
CH	Switzerland	LI	Liechtenstein	SI	Slovenia
CI	Côte d'Ivoire	LK	Sri Lanka	SK	Slovakia
CM	Cameroon	LR	Liberia	SN	Senegal
CN	China	LT	Lithuania	SZ	Swaziland
CS	Czechoslovakia	LU	Luxembourg	TD	Chad
CZ	Czech Republic	LV	Latvia	TG	Togo
DE	Germany	MC	Monaco	TJ	Tajikistan
DK	Denmark	MD	Republic of Moldova	TT	Trinidad and Tobago
EE	Estonia	MG	Madagascar	UA	Ukraine
ES	Spain	ML	Mali	UG	Uganda
FI	Finland	MN	Mongolia	US	United States of America
FR	France	MR	Mauritania	UZ	Uzbekistan
GA	Gabon			VN	Viet Nam

Title: Oxygen Sensor**DESCRIPTION**

This invention relates to an oxygen sensor, in particular to an oxygen sensor based on Galvanic Fuel Cell technology.

Oxygen sensors are used to monitor the concentration of atmospheric oxygen in a variety of clinical, industrial and commercial applications. One clinical application is the monitoring of oxygen in incubators for prematurely-born infants. Failure to maintain the correct partial pressure of oxygen in such an environment can lead to the patient being over- or under-oxygenated.

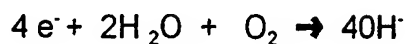
The effects of hypoxia and hyperoxia may be extremely serious, especially in premature infants, eg leading to brain damage and retinopathy respectively.

Fuel cell technology has been used as the basis of oxygen measurement in clinical applications for many years. Fuel cells offer an easy design solution, providing development engineers with a transducer that offers a small electrical signal directly proportional to the partial pressure of oxygen in the gas under measurement.

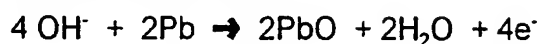
The Fuel cell is an electrochemical transducer or energy converter. The fuel cell, in the case of an oxygen sensor, is oxygen without which the cell will not operate. The fuel cell operates on the principle that oxygen is reduced at the sensing electrode, resulting in the generation of a current directly proportional to the number of oxygen molecules present in the electrolyte. The flow of oxygen molecules is controlled by a semi-porous plastic membrane. The rate of diffusion through this membrane is proportional to the partial pressure differential across it. Once diffused, the oxygen molecules dissolve into the electrolyte solution and migrate to the surface of the sensing electrode where they become absorbed to form an activated species capable of undergoing reduction.

Most commonly, the anode material is lead, in which case the general cell reactions are:

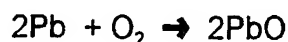
Sensing electrode (cathode)



Counter electrode (anode)



Overall cell reaction



As a result of the oxidation of Pb (anode material), four electrons are generated for every molecule of oxygen. These four electrons are then utilised for the reduction of oxygen at the cathode. It is this flow of electrons from one electrode to the other that constitutes an electric current. In the absence of oxygen, no oxidation can take place and no current is produced.

Oxygen sensors of the type described above suffer from the disadvantage that oxidation of the lead anode is not reversible, and when insufficient surface area remains for further oxidation, electron flow cannot be maintained. This causes the fuel cell to provide an output that is no longer proportional to the partial pressure of oxygen and therefore can no longer be relied upon. The period over which this erratic phenomenon occurs is dependant upon a number of factors including the way in which the anode is constructed.

Commonly, two or more substantially equivalent, independent sensors are used in combination to provide measurement and monitoring signals to the host equipment. Whereby the depletion of one of the cells outputs is used by the host equipment to provide the user with an indication that the measurement signal is no longer reliable. However, this results in notification to the user only after the period of unstable output has occurred and after one of the sensors has failed. Because the sensors are

inherently substantially equivalent and are experiencing identical environmental conditions and oxygen concentrations it not determinable which sensor will fail first.

There has now been devised an improved form of oxygen sensor which can overcome or substantially mitigate the above mentioned disadvantage.

According to the invention, there is provided an oxygen sensor comprising a measuring element and a monitoring element, each of which comprises a cell containing a cathode and an oxidisable anode, the cell having a membrane permeable to atmospheric oxygen, wherein the monitoring element is arranged to become depleted before the measuring element.

The oxygen sensor according to the invention is advantageous primarily in that depletion of the monitoring element provides an early warning of depletion of the measuring element, enabling the sensor to be replaced before such depletion of the measuring element. This significantly reduces the possibility of host equipment receiving a 'measuring' signal from a sensor or element of a sensor that is in its depletion phase and hence significantly reduces the attendant risk of hypoxia and hyperoxia.

Preferably, an electronic comparator circuit is provided to compare the output voltage of the measuring element and the monitoring element. The difference is preferably amplified and fed to comparators. Most preferably, a voltage difference of more than a first predetermined amount (eg a difference of more than 4%) triggers a visual or audio alarm, such as a warning lamp and/or a buzzer, to indicate to the user that the monitoring element is in depletion phase and that depletion of the measuring element is also therefore imminent. If the difference exceeds a (greater) second predetermined amount (eg 8%) then the control circuitry may entirely disable the apparatus.

Thus according to another aspect of the invention there is provided a method of monitoring the integrity of an oxygen measuring element comprising a cell containing

a cathode and an oxidisable anode, the cell having a membrane permeable to atmospheric oxygen, which method comprises:-

- a) providing a monitoring element similar to the measuring element but arranged to become depleted before the measuring element, and
- b) comparing the output voltages of the measuring element and the monitoring element.

The monitoring element may be arranged to become depleted before the measuring element by virtue of the monitoring element anode having a smaller surface area than that of the measuring element. For instance, relative to the measuring element anode the surface area of the monitoring element anode may be between 80% and 98%, more preferably between 90% and 98%, eg. about 95% for fuel cells designed to have a life expectancy of 400 000 oxygen percentage hours.

Where the measuring element and monitoring element cells differ in the surface area of the anode, they are preferably identical in all other respects such as the nature of the cathode, permeable membrane, electrolyte etc.

The anodes of the measuring element and the monitoring element are preferably of lead. The cathodes of the measuring element and the monitoring element are preferably of gold.

All components of the measuring element and the monitoring element, including the electrolyte, are preferably independent. Separation of the electrolytes of the two elements ensures that, during depletion of the monitoring anode, its cathode cannot derive ion flow from the measuring anode.

The measuring element and the monitoring element are preferably housed within a single unit, though they may alternatively be separate units mounted independently within the oxygenated environment.

The invention will now be described in greater detail, by way of illustration only, with reference to the accompanying drawings, in which:-

Figure 1 shows a schematic sectional side view of an oxygen sensor according to the invention;

Figure 2 shows schematically the outputs of the sensor of figure 1 during prolonged usage; and

Figure 3 shows an electronic comparator circuit in conjunction with the sensor of figure 1.

Referring first to figure 1, an oxygen sensor for use in clinical applications, eg in controlling the oxygen partial pressure in an incubator for premature babies, is generally designated (1).

The sensor (1) is divided into two compartments (2,3) by an internal barrier (4). Each compartment (2,3) constitutes a fuel cell and contains an identical gold cathode (5,6) and a lead anode (7,8). The cells (2,3) are filled with identical electrolyte solutions and have identical oxygen-permeable membrane windows (9,10) adjacent to the respective cathodes (5,6).

The cells (2,3) are identical save that the anode (8) of the right-hand (as viewed in figure 1) cell (3) has a surface area which is 95% that of the anode (7) of the left-hand cell (2). In use, oxygen molecules diffuse through the membranes (9,10), dissolve in the electrolyte and migrate to the surface of the respective cathodes (5,6) where they undergo reduction. The cell reactions are as given above and reduction of the oxygen is accompanied by oxidation of the lead anodes (7,8).

Initially, the rate of reaction in both cells (2,3) is the same and the output voltages of the cells (2,3) are substantially the same. However, after prolonged use the surfaces of the lead anodes (7,8) become progressively oxidised and the area available for further oxidation becomes depleted. In these circumstances, flow of electrons across

the cells (2,3) cannot be maintained. The output voltage of the cells (2,3) falls even where the oxygen concentration is constant.

Because the surface area of the anode (8) of the right-hand cell (3) is less than that of the left-hand anode (7), the anode (8) becomes depleted sooner than the other anode (7). Figure 2 shows typical plots of output voltage against time for the two cells (2,3) at constant oxygen partial pressure. Initially, the output voltages are adjusted, through compensation resistance where this is necessary, to be substantially equal and constant. When depletion of the right-hand anode (8) occurs, the output voltage (V_R) falls sharply (broken line in figure 2), as does the output voltage (V_L) of the left-hand cell (2) a short time later.

In the sensor (1) according to the invention, the left-hand cell (2) is used to measure the oxygen partial pressure in, for example, an incubator for premature babies. The rate of diffusion of oxygen through the membrane (9), and hence the output voltage of the cell (2) is proportional to the oxygen partial pressure within the incubator. The right-hand cell (3) is used to check the integrity of the measured oxygen partial pressure.

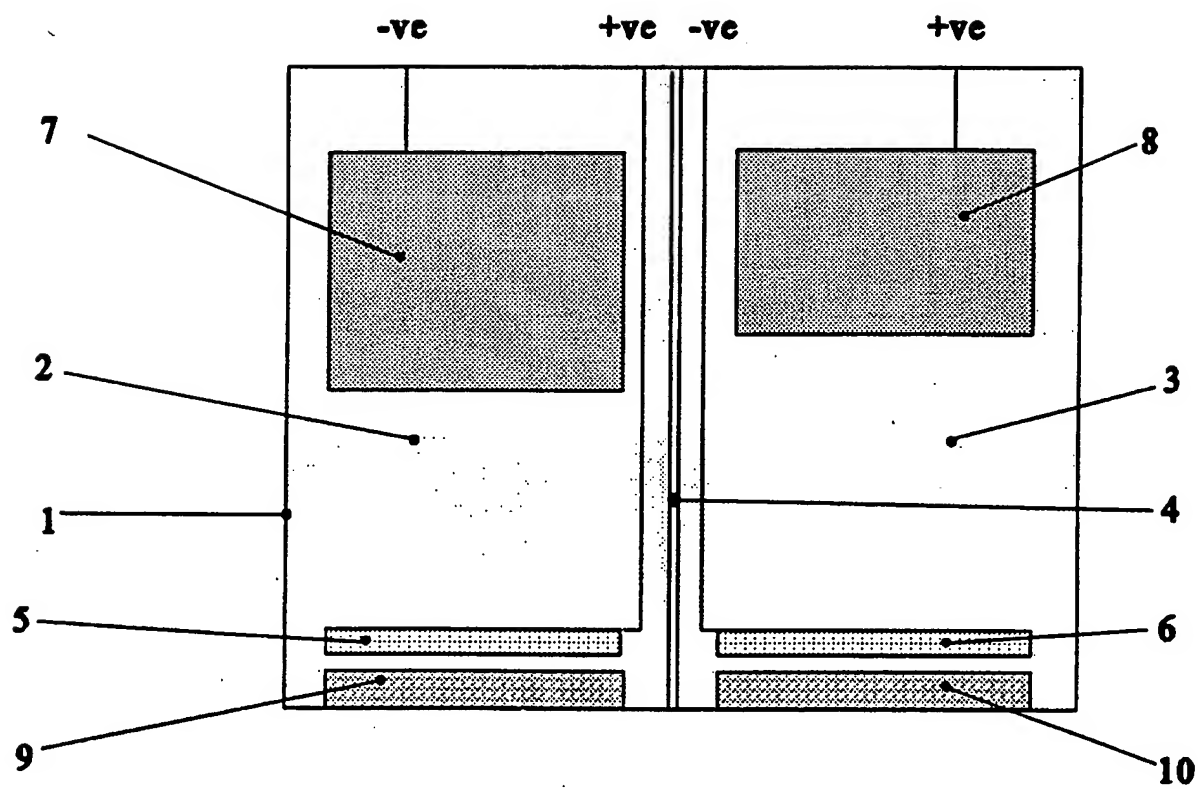
As shown in figure 3, the outputs of the cells (2,3) are fed to an amplifier (31) and the difference or error (e) is calculated. The error voltage is fed to a series of comparators (32,33) which compare the error (e) to a preset value, eg 4% of the amplified output of the left-hand cell (2). If the error (e) is less than the preset value then the output voltage V_R is used to control supply of oxygen to the incubator. Should the error (e) exceed the preset value then a lamp (34) is illuminated to indicate that depletion of the right-hand cell (3) has begun and depletion of the left-hand cell (2) is imminent. The user should at this point replace the sensor. If this is not done then the error (e) increases until a second preset value is reached (eg $e = 8\%$) at which the comparator (32) actuates a switch (35) which disables the sensor (1). The sensor (1) is thus useable whilst the error (e) is less than the first preset value. When that limit is exceeded (at the time t_{warn} shown in figure 2) a warning is given to the user, but the

sensor (1) remains operational for a short period until a time t_{off} (see figure 2) at which the error (e) exceeds the second preset value.

CLAIMS

1. According to the invention, there is provided an Oxygen sensor arrangement comprising of a measuring element and a monitoring element, each of which comprises a cell containing a cathode and an oxidisable anode, the cell having a membrane permeable to atmospheric oxygen, wherein the monitoring element is designed to become depleted before the measuring element.
2. An oxygen sensor as claimed in Claim 1, wherein the monitoring element anode has a smaller surface area than that of the measuring element.
3. An Oxygen sensor arrangement as claimed in Claim 1 wherein, the measuring and monitoring element are housed independently in separate units for mounting within the same oxygenated environment.
4. An Oxygen sensor arrangement as claimed in Claim 1 or Claim 2 or Claim 3 wherein, the failure of the monitoring element, through means of a suitable electronic comparator circuit, indicates to the user, at a predetermined point, the impending failure of the measuring element.
5. An Oxygen sensor arrangement as claimed in Claim 1 or Claim 2 or Claim 3 or Claim 4 wherein, the failure of the monitoring element, through means of a suitable electronic comparator circuit, disables the output of the measuring element at a predetermined point.
6. According to another aspect of the invention there is provided a method of monitoring the integrity of an oxygen measuring element comprising a cell containing a cathode and an oxidisable anode, the cell having a permeable membrane to atmospheric oxygen, wherein the monitoring element is similar to the measuring element but arranged to become depleted before the measuring element.

7. . An Oxygen sensor arrangement as claimed in Claim 6 wherein, the output voltages of the measuring element and monitoring are compared.
8. An oxygen sensor arrangement substantially as described herein with references to Figures 1 - 3 of the accompanying drawing.

**Figure 1**

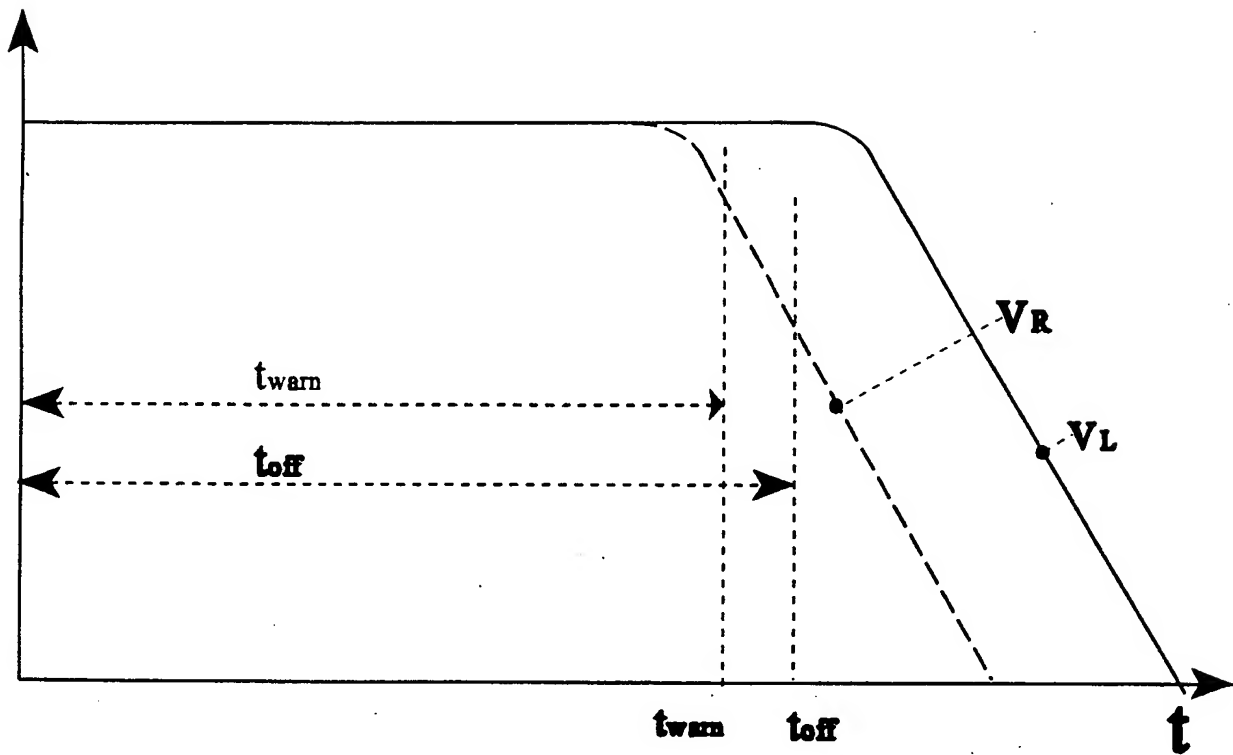
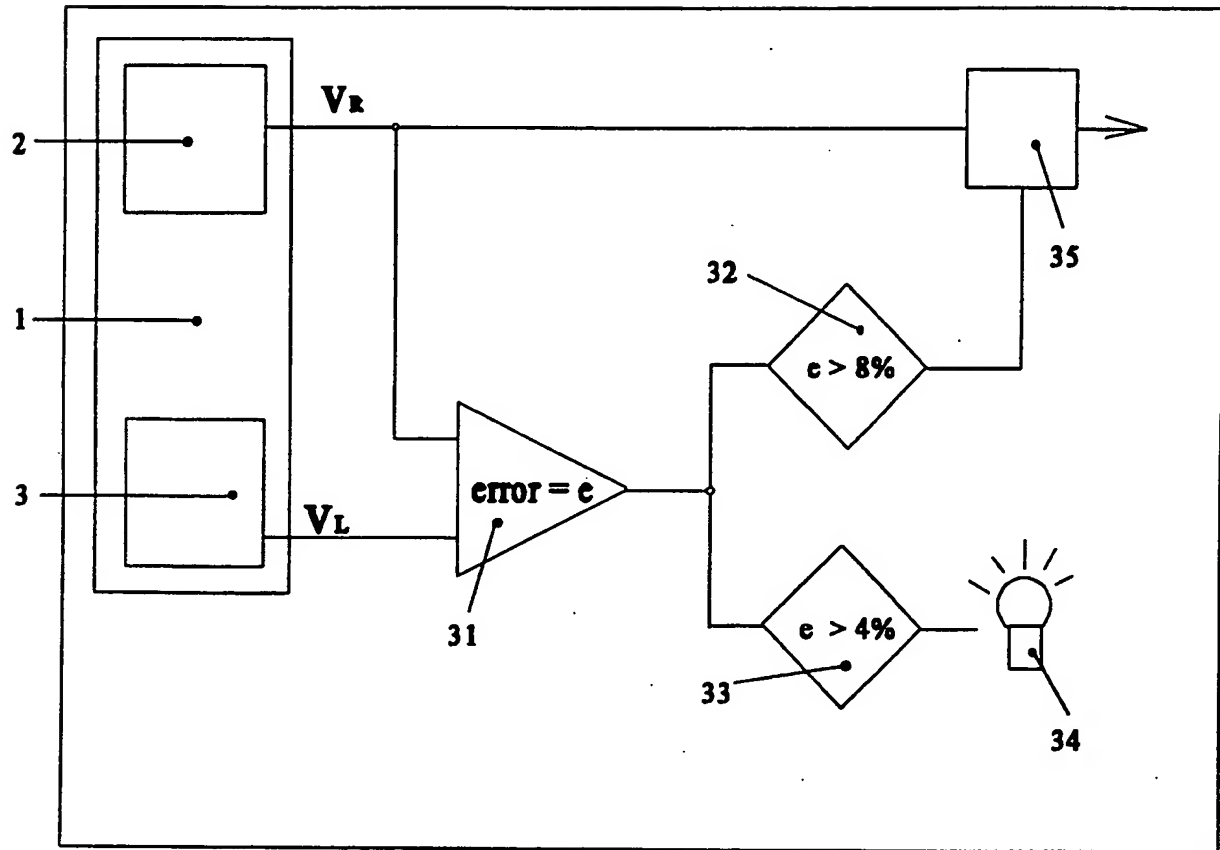


Figure 2

**Figure 3**

A. CLASSIFICATION OF SUBJECT MATTER
G 01 N 27/416

According to International Patent Classification (IPC) or to both national classification and IPC

B. FIELDS SEARCHED

Minimum documentation searched (classification system followed by classification symbols)
G 01 N

Documentation searched other than minimum documentation to the extent that such documents are included in the fields searched

Electronic data base consulted during the international search (name of data base and, where practical, search terms used)

C. DOCUMENTS CONSIDERED TO BE RELEVANT

Category *	Citation of document, with indication, where appropriate, of the relevant passages	Relevant to claim No.
P, A	GB, A, 2 284 059 (MICRO MEDICAL) 24 May 1995 (24.05.95), abstract; fig. 1. --	1.6
A	US, A, 5 262 034 (KUNZ) 16 November 1993 (16.11.93), claims; fig. 1-3. -----	1.6

☐ Further documents are listed in the continuation of box C.

☐ Patent family members are listed in annex.

* Special categories of cited documents:

- *A* document defining the general state of the art which is not considered to be of particular relevance
- *E* earlier document but published on or after the international filing date
- *L* document which may throw doubts on priority claim(s) or which is cited to establish the publication date of another citation or other special reason (as specified)
- *O* document referring to an oral disclosure, use, exhibition or other means
- *P* document published prior to the international filing date but later than the priority date claimed

- *T* later document published after the international filing date or priority date and not in conflict with the application but cited to understand the principle or theory underlying the invention
- *X* document of particular relevance; the claimed invention cannot be considered novel or cannot be considered to involve an inventive step when the document is taken alone
- *Y* document of particular relevance; the claimed invention cannot be considered to involve an inventive step when the document is combined with one or more other such documents, such combination being obvious to a person skilled in the art
- *&* document member of the same patent family

Date of the actual completion of the international search
26 July 1996

Date of mailing of the international search report

20.09.96

Name and mailing address of the ISA

European Patent Office, P.B. 3818 Patentlaan 2
NL - 2280 HV Rijswijk
Tel. (+31-70) 340-2040, Tx. 31 651 epo nl,
Fax: (+31-70) 340-3016

Authorized officer

NARDAI e.h.

ANHANG

zum internationalen Recherchen-
bericht über die internationale
Patentanmeldung Nr.

ANNEX

to the International Search
Report to the International Patent
Application No.

ANNEXE

au rapport de recherche inter-
national relatif à la demande de brevet
international n°

PCT/GB 96/01110 SAE 133908

In diesem Anhang sind die Mitglieder
der Patentfamilien der im obenge-
nannten internationalen Recherchenbericht
angeführten Patentdokumente angegeben.
Diese Angaben dienen nur zur Unter-
richtung und erfolgen ohne Gewähr.

This Annex lists the patent family
members relating to the patent documents
cited in the above-mentioned inter-
national search report. The Office is
in no way liable for these particulars
which are given merely for the purpose
of information.

La présente annexe indique les
membres de la famille de brevets
relatifs aux documents de brevets cités
dans le rapport de recherche inter-
national visée ci-dessus. Les renseigne-
ments fournis sont donnés à titre indica-
tif et n'engagent pas la responsabilité
de l'Office.

Im Recherchenbericht angeführtes Patentdokument Patent document cited in search report Document de brevet cité dans le rapport de recherche	Datum der Veröffentlichung Publication date Date de publication	Mitglied(er) der Patentfamilie Patent family member(s) Membre(s) de la famille de brevets	Datum der Veröffentlichung Publication date Date de publication
GB A1 2284059	24-05-95	GB A0 9322737	22-12-93
US A 5262034	16-11-93	JP A2 6236767	23-08-94